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SUBJECT: Chemical Feasibility of Homogeneous Neutron Poisons for Criticality Control in Fuel Reprocessing

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ABSTRACT

A preliminary examination has demonstrated the apparent chemical feasibility of the nuclear poisons, boron, cadmium, and rare earth elements, in the proposed flowsheet for reprocessing Consolidated Edison thorium reactor fuel. These elements remained in solution and were not volatilized to a significant extent during the feed adjustment step. In simulated dissolver solutions containing the poisons, 3% of the boron and less than 1% of the cadmium or rare earths were lost during boildowns. The solvent extraction of uranium with 2.5% TBP in Amsco from acid feed solutions containing sufficient nuclear poison to maintain a subcritical system, gave decontamination factors of 4,000, >500, and >3000 for boron, cadmium, and rare earths, respectively. Using acid deficient feed solutions, the corresponding factors were 9000, >1000, and $>15,000$. Single extraction cycles were made in which the concentrations of boron, rare earths, and cadmium in the uranium product were reduced to within the probable acceptable limits, i.e., 2.5 ppm, <4 ppm and <17 ppm, respectively.

NOTICE

DISCLAIMER

1.0 INTRODUCTION

This report presents the data obtained from studies made to determine the chemical feasibility of either boron, cadmium, or mixtures of samarium and gadolinium as homogeneous criticality controls in the feed adjustment and solvent extraction sections of the proposed method for reprocessing Consolidated Edison thorium reactor fuel. This fuel consists of 96% ThO_2-4% UO_2 (fully enriched uranium) in a stainless steel jacket. The primary objectives of these studies were to determine if sufficient concentrations of the nuclear poisons could be maintained during the feed adjustment cycle and to determine to what extent the poisons could be separated from the uranium during the solvent extraction cycle. This data plus other information will be presented to the Criticality Review Board to use in determining the applicability of these neutron poisons as criticality controls.*

Previous criticality studies made of the existing Thorex Pilot Plant[1] indicated that appropriate measures must be taken to prevent the possibility of collecting critical amounts of fissionable material during the processing of highly enriched solutions. Consequently, the incorporation of soluble salts having high neutron cross sections was suggested as a possible safety measure during the processing of Consolidated Edison fuel.[2,3] Although such soluble nuclear poisons have been suggested as reactor controls,[4,5,6] and as a safety measure in the reprocessing of slightly enriched uranium,[7] the chemical behavior of these compounds in the proposed reprocessing procedure was unknown.

The data reported here shows the materials are compatible under all conditions studied and they can be effectively separated from uranium. Further work will be done to examine the effect of other headend conditions and will be presented in future reports. The chemical behavior of the poisons during dejacketing and core dissolution is being investigated by L. M. Ferris and co-workers at ORNL. This data is included in the monthly progress reports for Section B, Chemical Technology Division. A final comprehensive ORNL report will be issued on completion of the testing program.

* At a recent meeting on criticality, it was stated that it may be necessary to use as much as 0.3 M boron or equivalent nuclear poison. This concentration would prevent criticality excursions that might occur because of unusual configurations of the slurry present during dejacketing and core dissolutions. Work is in progress to determine if these concentrations can be used.

Appreciation is expressed to H. Kubota, who developed analytical procedures for boron, and to the groups headed by G. R. Wilson and E. I. Wyatt for their analytical support. R. C. Lovelace assisted in performing some of the laboratory experiments.

2.0 FEED PREPARATION

2.1 Introduction

Previous papers,[8-13] although inconsistent, indicate that boric acid is volatilized to some extent from boiling solutions. In the feed adjustment step of the proposed flowsheet for reprocessing Consolidated Edison fuel elements, the dissolver solution is prepared by dissolving the 5% UO_2-95% ThO_2 pellets in 13 M HNO_3 containing 0.04 M NaF as a catalyst and 0.04 M $Al(NO_3)_3$. The solution is then evaporated to a boiling point of about 135°C. At this temperature, assuming the fuel had no burnup, a solution 4 M Th, 64 g/l U, and 2 M HNO_3 is obtained. If no credit is taken for the neutron capture by the nonfissionable components of the solutions, the loss of boron during this evaporation must be sufficiently low that equimolar concentrations of B^{+3} and U-235 can be maintained for the solution to remain subcritical.

2.2 Boron Volatility Studies

Laboratory experiments indicate that the loss of boron during the headend boildown is negligible (Table 1). The maximum loss occurred when a simulated dissolver solution was purposely allowed to proceed to 181°C, a temperature in excess of that obtainable in the pilot plant using the maximum steam pressure in the heating jacket of 120 pounds per square inch. Six per cent of the boron was lost to the distillate during this run whereas only 2-3% is lost during a normal boildown (130-140°C). The fractions of boron lost by physical entrainment and by volatilization in the step is not known.

The losses of cadmium and rare earths found in similar experiments amounted to less than 0.5%.

3.0 SOLVENT EXTRACTION CYCLE

3.1 Introduction

Soluble poisons that are present in the feed solution are separated from the uranium during the solvent extraction cycle of the proposed flowsheet. The extractant will be 2.5% TBP in Amsco and will contain about 8 grams of uranium per liter. The solvent will be safe by virtue of its concentration since 2.5% TBP is saturated at 11 grams of uranium per liter.

Table 1. Volatility of Boron During Evaporation of Dissolver Solutions

Run Number	1	2	3	4	5	6	7
Initial Solution Composition, M							
Boron	0.1	0.1	0.2*	0.036	0.2	0.048	0.03
HNO_3	-	8.5	8.2	8.2	8.2	4.4	8
U	-	-	0.06	0.06	0.06	0.02	0.06
Th	-	-	0.95	0.89	0.95	0.5	1
$Al(NO_3)_3$	-	-	-	0.04	0.04	0.04	0.04
NaF	-	-	-	0.04	0.04	0.02	-
Initial Volume, mls	500	500	500	520	500	2000	500
% of Original Volume After Distillation	5	5	51	37	25	13	5
Maximum Aqueous Temperature, °C	101	120.5	119.5	135	138	142	181
By Analysis							
% of the Boron Remaining in Residue	95	96	>99	97	93	>98	94
% of the Boron in Distillate	<1	3.6	<1	3	2	2	6

* Boron added as $Na_2B_4O_7$. All other runs used H_3BO_3.

The exact specifications for the final uranium product is not known. Based on other specifications, a probable value for the nuclear poisons is 8 ppm or less of boron or thermal neutron absorption equivalent per gram of uranium. The decontamination factors obtained using either an acid or acid deficient flowsheet indicate that one to two solvent extraction cycles should reduce the contaminants to the desired level.

3.2 Acid Flowsheet

3.2.1 Boron Decontamination. Boron decontamination factors of 3×10^3 to 4.4×10^3 with acceptable thorium decontamination factors and uranium losses were obtained by solvent extraction of acid feeds using the conditions described in Table 2. The slight effect produced by the presence of boron in the scrub is probably within the limits of accuracy of the analytical procedure. There was no difference observed in the separation of boron from uranium when the $Al(NO_3)_3$ concentration of the scrub was increased from 0.75 M to 1.0 M.

A batch strip made on the organic product of run #1, Table 2, with 0.008 M $Al(NO_3)_3$ gave a product solution of the desired purity. The composition corresponded to 2.5 ppm of boron per gram of uranium metal.

The most suitable conditions for the second cycle solvent extraction section of the flowsheet have not been determined. Preliminary experiments gave boron decontamination factors ranging from 1800 to 3500 (Table 3).

Table 2. Separation of Boron from Uranium Using the Acidic Flowsheet

Feed: 0.064 M U, 1 M Th, 1.28 M $Al(NO_3)_3$, 0.04 M NaF, 0.9 M HNO_3, 0.096 M H_3BO_3

Extractant: 2.5 V % TBP in Amsco 125-82
Flow Rate: 1 feed, 0.5 scrub, 3 extractant
5 Extraction Stages; 6 Scrub Stages

Run Numbers	1	2	3
M of $Al(NO_3)_3$ Scrub Solution	0.75	1.00	0.75
M of Boron in Scrub Solution	-	-	1.0
No. of Equilibrations	43	31	31
% of U Lost in Aqueous Waste	0.04	0.01	0.09
Thorium DF	3,300	8,300	>13,000
Boron DF	4,400	4,200	3,070
Calculated ppm B in Uranium Metal	16	20	23

Table 3. Separation of Boron from Uranium in the Second Extraction Cycle

2.5 V % TBP in Amsco 125-82
Flow Ratio - 1 Feed, 0.5 Scrub, 3 Extractant
3 Extraction Stages, 4 Scrub Stages, except where noted *

Run Numbers		1	2	3*
Feed Composition M:	U	0.034	0.023	0.055
	HNO_3	2.0	3.10	4.10
	$Al(NO_3)_3$	0.77	1.05	~0.006
	H_3BO_3	0.05	0.043	0.087
M of $Al(NO_3)_3$ Scrub Solution		0.75	1.0	1.0
No. of Equilibrations		17	17	16
U Lost in Aqueous Waste		0.69	0.14	1.17
B DF		1940	3550	1800
Calculated ppm B in Uranium Metal		36	25	40

* 4 extraction stages - 5 scrub stages 0.4 g/l Th also present.

3.2.2 Cadmium Decontamination. A repetition of the first boron run (Run 1, Table 2) using a feed containing 0.03 M cadmium nitrate in place of the boron, gave a decontamination factor of >480 for cadmium. The loss of uranium to the aqueous was 0.08% and the separation factor between uranium and thorium was >14,000. A batch strip of this organic product with 0.008 M $Al(NO_3)_3$ produced a solution containing an acceptable concentration of cadmium, <17 ppm per gram of uranium.

3.2.3 Rare Earth Decontamination. A rare earth decontamination factor greater than 3000 was obtained in a test similar to the ones made with cadmium and boron. In this experiment the feed was poisoned with 1 g per liter of Lindsay #903 rare earth oxide. This oxide contained about 63 per cent samarium and 23 per cent gadolinium oxide. Cerium-141 and Europium 152-154 were present in tracer quantities to follow the course of the rare earths. A decontamination factor of >4300 was obtained for the cerium and >3200 for the europium. Agreement between these two values is within the accuracy of the analysis. A more accurate analytical method is necessary to determine the exact concentration of rare earths in the uranium product.

3.3 Acid Deficient Flowsheet

3.3.1 Boron Decontamination. A decontamination factor of 9,200 for boron was obtained in a countercurrent extraction using the following conditions; feed, 0.062 M U, 1.49 M Th, 0.1 M H_3BO_3, 0.033 M acid deficient, 1.6 M $Al(NO_3)_3$; extractant, 2.5% TBP in Amsco; scrub, 0.1 M H_3BO_3, 0.04 M acid deficient, 1.24 M $Al(NO_3)_3$. Nineteen equilibrations were made using five extractant and six scrub stages with a feed/scrub/extractant ratio of 1/0.5/3. The loss of uranium to the aqueous waste was 0.03% and the thorium decontamination factor was 3300. The boron in the product had been reduced to the acceptable level of 8 ppm of boron per gram of uranium.

Through error the feed was 1.6 M $Al(NO_3)_3$ rather than the desired 1.2 M. This concentration of aluminum nitrate caused some crystallization at room temperature and necessitated keeping the feed slightly warm during the solvent extraction.

3.3.2 Cadmium Decontamination. A decontamination factor greater than 1000 was obtained for cadmium in an acid deficient countercurrent extraction. This experiment used the same condition as the boron run described above except the feed was adjusted to a lower aluminum concentration. The final feed solution contained 0.05 M U, 1.2 M Th, 0.04 M AD, 1.3 M $Al(NO_3)_3$ and 0.027 M $Cd(NO_3)_2$. The thorium separation factor obtained with this feed was 550 and the uranium loss to the aqueous waste stream was 0.005%.

In this experiment the exact concentration of the neutron poisons in the uranium product was not determined.

3.3.3 Rare Earth Decontamination. A countercurrent extraction identical to the boron experiment described above was made with the feed poisoned with 1 g/l of Lindsay Code #903 rare earth oxides and spiked with Europium-152-154 and Cerium-141 tracer. A decontamination factor >8,000 was observed for the cerium and >15,000 for the europium. The organic product contained < 4 ppm of rare earths per gram of uranium.

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